Preliminary Tests for Grafting p-Nitrophenyl on Carbon Nanotubes

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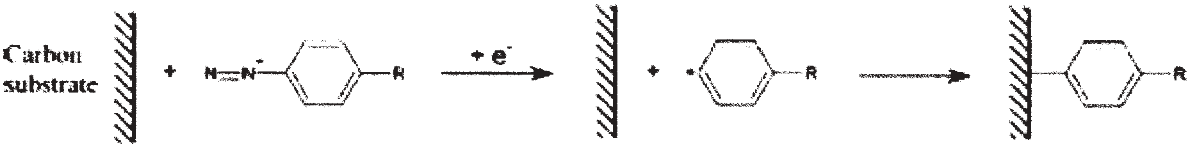
Experiments concerning the reduction of diazonium ion to radical species realized on glassy carbon and platinum electrodes allowed p-nitrophenyl grafting on the electrode surfaces electrochemically and by immersion. The grafting has been tested electrochemically in order to find the degree of surface coverage by i) cycling voltammetry of the grafted electrode in CH_3CN *containing 0.1 mol* L^{-1} $TBABF_4$ *in the field of potential characteristic for the activity of the nitro groups reduction and/or by ii) cycling the grafted electrode in a transfer solution containing ferrocene in 0.1 M* $TBABF_4$*,* CH_3CN*.*

Keywords: p-nitrobenzenediazonium tetrafluoroborate, electrografting, grafting by immersion

Numerous examples for the derivatization of carbon electrode materials have been reported because of their importance in electrocatalysis, in electroanalysis, and in biological sensing [1]. Traditionally, pathways for modifying carbon have involved coating the surface with a polymer film or derivatizing the existing or oxidatively generated surface-bound functional groups (e.g., carboxyl, alcohol, and quinone) [2,3]. Recently, several schemes have been introduced to bind moieties directly to the carbon lattice [4-6]. One of the simplest, most flexible, and promising of these methods involves the attachment of functionalized aryl groups via the electrochemical reduction of the corresponding diazonium salt. Savéant and Pinson were the first to demonstrate that the reduction of an aryl diazonium cation afforded the corresponding aryl radical, which can further react with a carbon atom of the carbon substrate to yield the covalent bonding of this aryl group according to scheme 1 [4]. Pinson and Andrieux have demonstrated that the generation of the aryl radical is a concerted process, which involves the electron transfer and the cleavage of dinitrogen before the formation of the covalent bond [7]. This modification procedure is very attractive because it allows the presence of selected functions on the aryl groups.



Scheme 1

Taking into account the latest achievements in the field of modified electrodes as well as the increased potentiality of carbon nanotubes which have novel structural electronic and mechanical properties, the research in this paper was dedicated to the grafting of a model compound – p-nitrophenyldiazonium tetrafluoroborate. Our approach focused on functionalization of glassy carbon and platinum electrodes as a previous step for the functionalization of single-walled carbon nanotubes (SWCNTs).

Experimental part

The investigated substrate *p*-nitrobenzenediazonium tetrafluoroborate (97%, Aldrich) was used as received and kept in the freezer. Anhydrous (99.8%) acetonitrile (Aldrich) was used as received. Tetra-*n*-butylammonium tetrafluoroborate (99%, Aldrich) was dried under vacuum at 60°C for 3 days. Distilled water was obtained from an Elgastat water purification system (5 MΩ cm).

The electrochemical studies were carried out using a Bio**Logic** model EC-Lab®V9.25 potentiostat/galvanostat with 5 channels. All electrochemical experiments were performed in milimolar organic or aqueous solutions containing a supporting electrolyte using conventional three-electrode cells.

The working electrodes were platinum (Pt), glassy carbon (GC) or modified (see below) glassy carbon disks ($\Phi = 3$ mm); the counter electrodes were platinum wires and a Ag/10 mM $AgNO_3$, 0.1 M tetra-n-butylammonium tetrafluoroborate electrode served as reference. In organic solutions, all potentials were given *vs* this Ag/Ag^+ electrode whose potential was 0.56 V *vs* NHE (-0.07 V *vs* Fc/Fc^+).

The solutions were degassed with argon for 20 min before each measurement and kept under argon atmosphere during the entire experimental period. All experiments were run at 25°C.

The electrochemical studies in organic media were carried out by cyclic voltammetry (CV), controlled potential electrolysis (CPE) and square wave voltammetry (SWV) in milimolar solutions of substrates in acetonitrile (CH_3CN) containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$).

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The electrochemical grafting was performed by potentiodynamic (CV) and potentiostatic (CPE) methods in milimolar solutions of substrates in CH_3CN containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$). The grafted GC electrodes were denominated as *Nb*GC.

Grafting by immersion was performed at open circuit by dipping the GC electrode for a given time (typically 10 min) into 2 mL of a milimolar solution containing the given substrate (see results and discussion section). The electrode was removed from the immersion solution and washed thoroughly with acetone and dried with fine paper (two times). Finally, the electrode was transferred in a flask with 2 mL of CH_3CN, sonicated for 10 min, and analysed.

The grafting degree was checked by two methods:

i) cycling voltammetry (CV) of the grafted electrode in CH_3CN containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$) in the field of potential characteristic for the activity of the nitro group and/or by

ii) cycling the grafted electrode in a transfer solution containing ferrocene (electrochemical probe) in 0.1 M $TBABF_4$, CH_3CN (CVFc).

Results and discussion

With the aim of functionalizing SWNTs with organic molecules for biological applications we tested the reduction of *p*-nitrobenzenediazonium tetrafluoroborate (PNDB) on glassy carbon taking into account its low porosity and structural similarity with SWNTs. The electrochemical study of *p*-nitrobenzenediazonium tetrafluoroborate allowed the establishment of the electrode potential to be used for electrodeposition and the electrochemical domain for characterisation of the grafted electrode. Grafting of *p*-nitrobenzene was performed by electrochemical methods (CV and CPE) and by immersion. Grafting was evaluated using the signal for reduction of *p*-nitrobenzene grafted on the glassy carbon electrode.

Figure 1 shows the CVs obtained for a Pt electrode in 1 mM PNBD when different scan rates are used. A first cathodic peak around – 0.1 ÷ – 0.2 V (depending on the scan rate) attributed to the diazonium reduction followed by the reversible cathodic wave at –1.5 V corresponding to the reduction of the nitro group to the radical anion can be observed (table 1). The oxidation wave observed on the return sweep is attributed to the oxidation of the radical anion. This second process is reversible only in anhydrous solutions and it is strongly influenced by the residual water which turns it to an irreversible process.

Similar results have been obtained on Pt and GC electrodes. The diazonium reduction peak is shifted to a more negative value (-0.4 V) on glassy carbon electrode (fig. 2) in comparison with platinum.

The fact that the first voltammetric wave is irreversible indicates that an irreversible reaction (i.e. the cleavage of dinitrogen) is associated with the electron transfer. On the second scan this wave disappears completely. This is an indication of the surface blocking by the organic groups which became attached to the surface (fig. 3).

This behaviour of the diazonium salt is related both to its easy reduction (which is itself connected with the very strong electron-withdrawing character of the diazonium group) and to the concertedness of the electron transfer – dinitrogen cleavage which ensures that the formation of the radical takes place “on the surface” itself. At the very

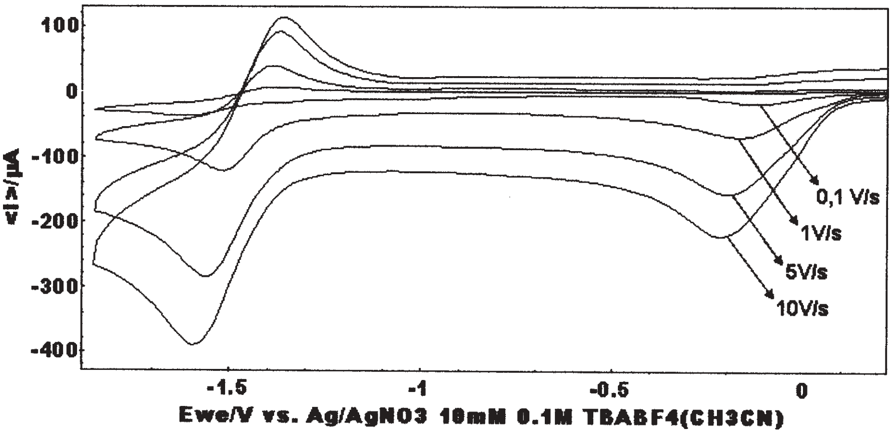

Fig. 1. CVs on Pt in 1mM PNBD solution in 0.1M $TBABF_4$, CH_3CN at different scan rates: 0.1 V / s; 1 V/s; 5 V/s; 10 V/s; 1st cycle

Table 1
ELECTROCHEMICAL DATA OBTAINED FROM CVs ON Pt IN 1mM PNBD SOLUTION AT DIFFERENT SCAN RATES

	Diazonium reduction		NO_2 reduction					
Scan rate (V/s)	Epc' (V)	Ipc' (µA)	Epc (V)	Ipc (µA)	Epa (V)	Ipa (µA)	Ef (V)
0.1	-0.121	-18.5	-1.61	-38.5	-1.38	5.81	-1.5
1	-0.167	-71	-1.51	-125	-1.39	38.6	-1.45
5	-0.193	-159	-1.56	-284	-1.37	93	-1.47
10	-0.216	-222	-1.59	-390	-1.36	114	-1.48

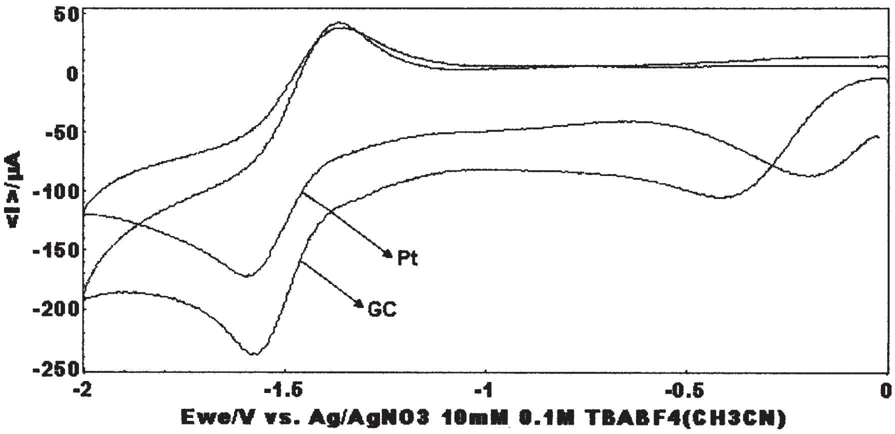

Fig. 2. CVs(1 V/s, 1st cycle) in 2mM PNBD solution in 0.1M $TBABF_4$, CH_3CN at platinium (Pt) and glassy carbon (GC) electrodes

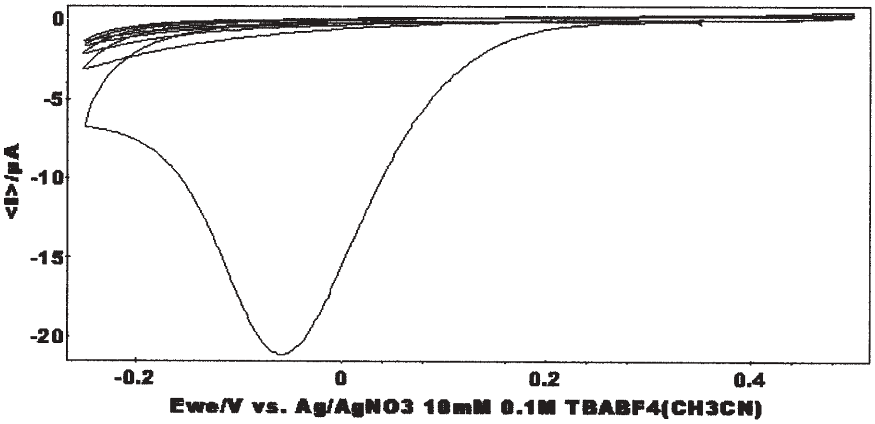

Fig. 3. Influence of cycling on the diazonium reduction in 7 mM PNBD (0.1 V/s, Pt)

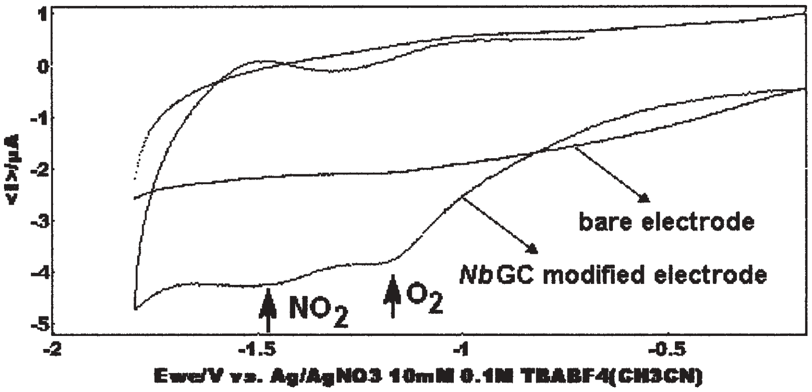

Fig. 4. CVs (0.1 V/s) of NbGC modified electrode (obtained by short CV, in 7 mM PNBD solution, 0,1 V/s) vs bare electrode

low cathodic reduction potential of the diazonium, the phenyl radical is not reduced and can react with the surface.

The modification of the electrode can be made also by the successive potential scanning in the potential range (0, -2). The CVs for obtaining the NbGC1 modified electrode as well as in the short potential range, showed that the associated response with the diazonium reduction disappears. A cathodic shift of the peak corresponding to the nitro group reduction to the radical anion can be also seen.

The voltammetric response during *p*-nitrobenzene electrografting consisting in the disappearance of the irreversible response associated with the diazonium salt reduction and the reversible response related to the nitrobenzene reduction can be translated, finally as an irreversible response due to the modification of the electrode by electrografting of nitrobenzene. This deposit is less conductive than the electrode and, as a consequence, the electrochemical behaviour of this modified electrode is the one of a blocking electrode. In other words, the cathodic response represents a mixture of the NO_2 electroactivity in solution and the electroactivity of the NO_2 immobilized groups.

Grafting by electrochemical methods

The electrochemical grafting was performed using potentiodynamic (CV) and potentiostatic (CPE) methods in milimolar solutions of substrates in CH_3CN containing 0.1 M $TBABF_4$.

Grafting by the potentiodynamic method (CV)

The grafting was performed by cycling the electrode potential in two ranges: a short range (0.5 V ÷ -0.45 V) and a long one (0.5 V÷ -2 V). The CV responses of the grafted electrodes after they were transferred in supporting electrolyte solution are shown in figure 4 and figure 5, respectively.

The voltammetric signal of the nitrophenyl group can be observed around -1.5 V (fig. 4). The cathodic and anodic peaks are located at the same potential leading to the conclusion that the *p*-nitrophenyl group is attached to the surface. The voltammetric wave that appears at -1.2 V is due to electroactivity of the O_2 traces (difficult to remove completely from the transfer solution).

In the case of the grafted electrode prepared by potential scanning on the long range (0.5 V÷ -2 V) after the transfer in the solution containing only the solvent and supporting electrolyte (CH_3CN + 0.1 M $TBABF_4$) the voltammetric

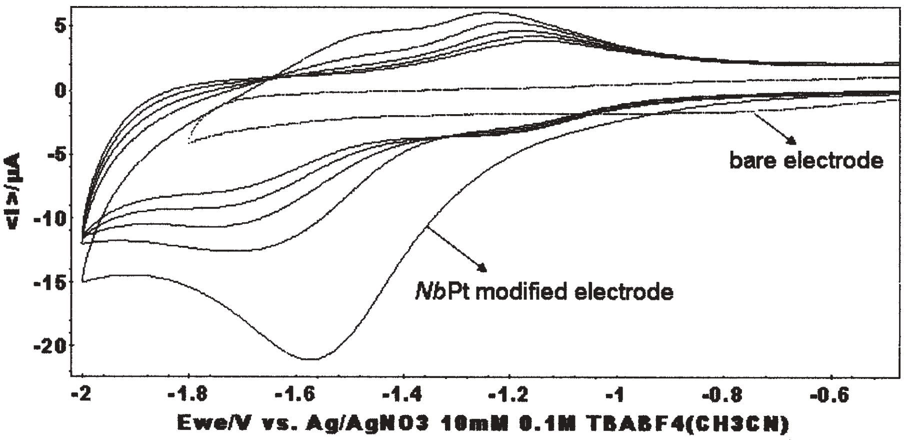

Fig.5. CVs (0.1 V/s, 5 succesive cycles) of NbPt modified electrode (obtained by long CV, 10 cycles, 0.1 V/s in 1 mM PNBD solution) vs bare electrode

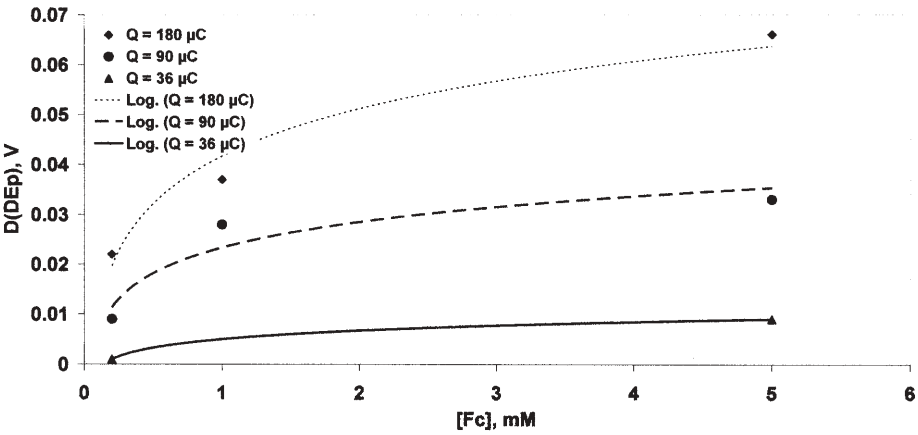

Fig.6. Variation of the ΔEp for ferrocene on grafted electrodes obtained from 1 mM PNBD solution by CPE at - 1.2 V at: 180 µC; 90 µC; 36µC

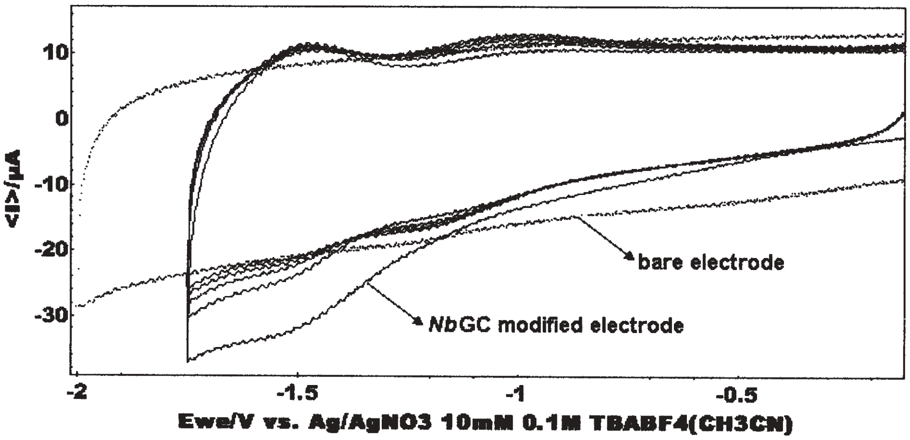

Fig.7. Succesive CVs of NbGC modified electrode (immersion for 30 min in 1mM PNBD solution in CH_3CN) vs bare electrode

signal of the nitrophenyl group can be also observed (fig. 5). Upon repetitive scans, this reversible wave rapidly disappears due to the protonation of the radical-anion of the *p*-nitrophenyl group by residual water. The presence of the peaks attributed to oxygen traces can be also observed (around -1.2 V).

Grafting by potentiostatic method (CPE)

The electrochemical grafting was performed by CPE in milimolar solutions of *p*-nitrophenyldiazonium tetrafluoroborate in CH_3CN containing 0.1 M $TBABF_4$ at the potential of –1.2 V using different cathodic charges.

The electrodes were transfered in the 0.1 M $TBABF_4$, CH_3CN solution or in ferrocene solutions in 0.1 M $TBABF_4$, CH_3CN and analysed according to the described procedures. The influence of the glassy carbon electrode modification conditions on the cyclic voltammetry response of ferrocene as electrochemical probe was investigated for layers grafted with different charges and for different ferrocene transfer solutions (fig. 6). Similar results have been obtained for the first and subsequent cycles (cycling between –0.25 and 0.3 V; 0.1 V/s).

From figure 6 it can be observed that the sensitivity of the electrochemical probe to the nitrobenzene deposit increases with the amount of charge passed during the electrochemical grafting and with the ferrocene concentration. Increased concentrations of the ferrocenne evidence a limitation by diffusion.

Grafting by immersion

Some results concerning the grafting of diazonium salts on glassy carbon and metals (iron, zinc, copper, nickel) without electrochemical induction have been reported in recent papers [8,9]. This spontaneous grafting has been also observed on silicon [10], gallium arsenide (GaAs), palladium [10], carbon black and carbon nanotubes [11,12]. Compared to the electrochemical grafting, this procedure provides a simpler and more versatile method for the elaboration of organic layers attached to the substrate. The grafting of aryl groups takes place on carbon substrates by dipping the substrate into an appropriate

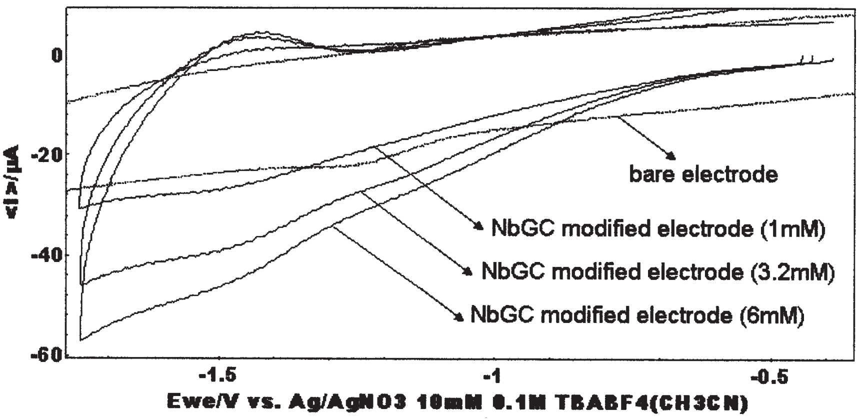

Fig.8. CVs (1V / s) obtained for NbGC modified electrodes by 10 min immersion in different PNBD concentrations: 1 mM; 3,2 mM; 6mM vs. bare electrode

diazonium salt solution. The presence of arylgroups on the substrate after its immersion into a diazonium salt solution in acetonitrile can be demonstrated by cyclic voltammetry in a supporting electrolyte solution where the signature of the nitrophenyl groups could be observed (after a through rinsing and sonication in CH_3CN of the electrode).

Modification of the electrodes without electrochemical induction was first accomplished by immersing samples in diazonium solutions of different concentration in CH_3CN for different periods of time. After immersion, the reacted electrodes were rinsed as described in Experimental and then transferred into a 0.1 M $TBABF_4$, CH_3CN solution for electrochemical tests. Grafting of diazonium salt on the surfaces was ascertained through the observation of the electrochemical system of nitrophenyl groups in acetonitrile solution as already reported in the literature [13]. Figure 7 shows cyclic voltammograms obtained on the GC electrode surface, before and after immersion in the 1 mM PNBD solution for 30 min. Regardless the concentration of the solution (fig. 8) or the immersion time, the voltammograms acquired after immersion exhibit a similar cathodic process at about -1.5 V. This cathodic process corresponds to the reduction of nitrophenyl groups grafted to the surface into the corresponding radical anions. This process is followed by other stabilization reactions (protonations, etc.) and the radical anions electrooxidation during the reverse scan. These reactions could explain the decrease of the CV response of the grafted electrode by cycling.

Conclusions

The functionalization of glassy carbon electrodes has been performed as a previous step for the functionalization of single-walled carbon nanotubes. It was observed that the attachment of the *p*-nitrophenyl group can be done either by electrochemical reduction or by dipping the glassy carbon or Pt surface in a solution of the diazonium salt, without potential or current control. The resulting organic layers are strongly attached to the surface as they resist sustained ultrasonic rinsing in acetonitrile. The grafting has been checked by electrochemical methods. The evolution of grafting degree has been followed in different grafting conditions (substrate concentration, electrodeposition charge and potential, immersion time).

The electrode coverage is lower with the layers obtained by chemical method than that obtained by electrochemical reduction of the diazonium salt solution. But these chemical layers could find applications in electroanalysis. The layers obtained from spontaneous grafting are of little use for a protective barrier (against corrosion, against diffusion of species, etc.), but they could find applications in systems where a very compact coverage of the surface is not necessary such as attachment of enzymes.

The influence of the glassy carbon electrode modification conditions on the cyclic voltammetry response of ferrocene as electrochemical probe was investigated for layers grafted with different charges. The sensitivity of the electrochemical probe to the nitrobenzene deposit increases with the amount of charge passed during the electrochemical grafting and with the ferrocene concentration. Increased concentrations of the ferrocenne evidence a limitation by diffusion.

Acknowledgments: Financial support from FP 6 Marie Curie Host Fellowship for the Transfer of Knowledge contract NANOTEC-EST MTKD-CD-2004-014059 is gratefully acknowledged.

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Manuscript received: 5.06.2007